

# Soft x-ray emission study of chromium hexacarbonyl

J.-H. Guo<sup>1</sup>, C. S  the<sup>1</sup>, A. F  lisch<sup>1</sup>, J. Nordgren<sup>1</sup>, L. Yang<sup>2</sup>, and H.   gren<sup>2</sup>

<sup>1</sup>Department of Physics, Uppsala University, Box 530, 751 21 Uppsala, Sweden

<sup>2</sup>Department of Physics and Measurement Technology, Link  ping University, 581 83 Link  ping, Sweden

## INTRODUCTION

We use a transition metal compound as a bridge between the free and the surface adsorbed species for the interpretation of core electron spectroscopies. Calculations for this purpose are carried out for carbon and oxygen x-ray absorption, x-ray emission and x-ray core electron shake-up spectra for Cr(CO)<sub>6</sub>. A detailed analysis of spectra are made with some previous assignment being revised [1].

## EXPERIMENT

The x-ray emission experiment was carried out at beamline 7.0 of Advanced Light Source, Lawrence Berkeley National Laboratory. This beamline [2] is comprised of a 5 m, 5 cm period undulator and a 10.000 resolving-power spherical grating monochromator. The beamline provides high flux and is capable of focusing the radiation with post-focusing mirrors to a narrow beam at the interaction region.

The soft x-ray emission was recorded using a high resolution-grazing incidence-grating fluorescence spectrometer [3]. The spectrometer provides a choice of three different spherical gratings. It has an entrance slit with adjustable width and uses a two-dimensional detector that can be translated to the focal positions defined by the Rowland circle of the grating in use. In these experiments a slit of 15   m and 30   m were selected and gratings with 5m radii and 400 and 1200 lines/mm were used to record the carbon and oxygen *K* emission, respectively. The estimated resolution at full width at half maximum (FWHM) was about 0.3 eV and 0.50 eV, respectively.

The Cr(CO)<sub>6</sub> molecule was contained in a gas cell with thin windows transmitting most of the radiation. The synchrotron radiation entered the cell through a 1600    thick silicon nitride window and the interaction region was viewed by the spectrometer through a 1600    thick polyimide window, supported by a polyimide grid and coated with 150    aluminium nitride [4]. The gas pressure was optimized so that most of the fluorescence was absorbed in the view region of the spectrometer. In the spectra presented here the pressure ranged from 0.7 mbar to 1.7 mbar.

## RESULTS

The C and O *K* x-ray emission spectra are presented in Figure 1. As one can expect from the one-center picture, the non-resonant x-ray emission spectra (NRXES) are dominated by CO outer valence B band. The CO-localized "4  " orbital turn up mostly in the oxygen spectrum, while the chromium *3d* band has low intensity in both spectra. One notes that the 8t<sub>1u</sub> (5  ) level is very strong in the carbon spectrum, while the oxygen spectrum is dominated by the 1   derived peaks, which makes the main feature in the oxygen spectrum narrower. Thus much of the signatures of the free CO spectra remain in the spectrum of Cr(CO)<sub>6</sub>, as actually they do also for the COCu<sub>N</sub> clusters [5]. A difference is that the 5   derived levels (as 8t<sub>1u</sub> and 5e<sub>g</sub>) are mostly of lower energy than the 1   derived levels (1t<sub>2u</sub>, 1t<sub>2g</sub>, 7t<sub>1u</sub>) while they reverse in order for the COCu<sub>N</sub> clusters and for CO/Cu(100).

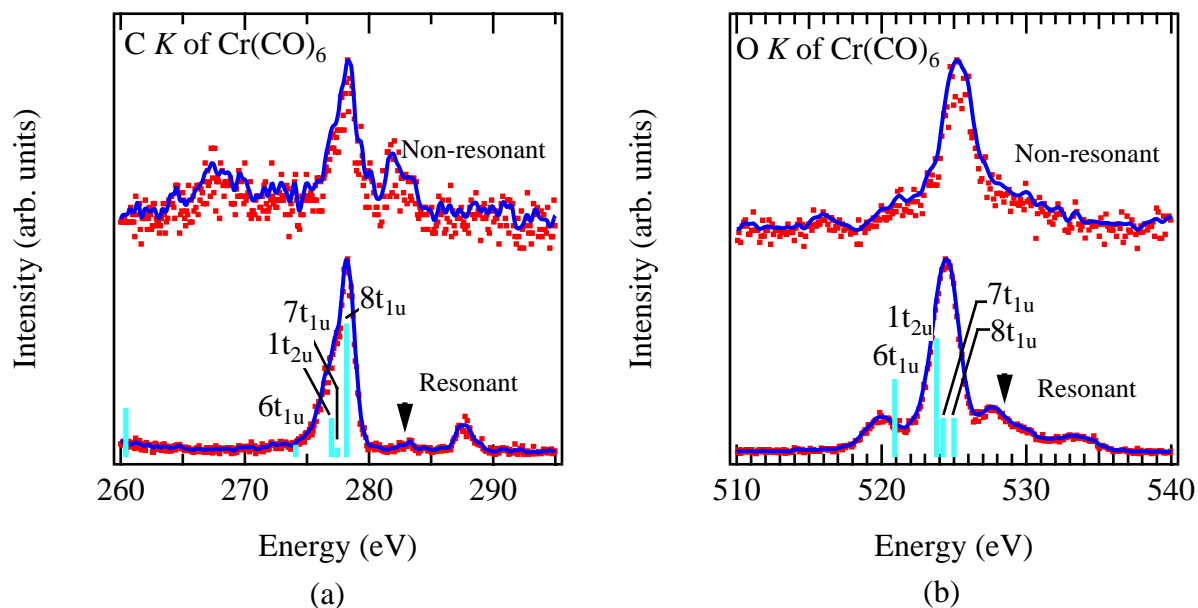


Figure 1. X-ray emission spectra of  $\text{Cr}(\text{CO})_6$  at C  $K$ -edge (a) and O  $K$ -edge (b).

The resonant x-ray emission spectra (RXES) were recorded by tuning the incident x-ray energy to the LUMO  $9t_{1u}\pi^*$  MO at  $h\nu = 287.5$  and  $533.9$  eV for C  $1s$ , respectively, O  $1s$  excitations, which comes out as an elastic peak in the spectra (see the bottom curves). Unlike for non-resonant spectra, symmetry selection operates for RXES, and can in principle be used for symmetry probing of occupied or unoccupied MO levels [6].  $\text{Cr}(\text{CO})_6$  belongs to the  $O_h$  point group in the ground state, and when the incident x-ray is tuned to  $9t_{1u}$ , only electrons occupying the ungerade MO's can fill the C  $1s$  or O  $1s$  hole orbitals according to dipole selection rule. Thus the RXES spectra are in principle sparser than the NRXES counterparts. There is, of course, still an open question how strong the symmetry-breaking Jahn-Teller effects operating between near-degenerate core excited are, and so if the core excited state really maintains the same symmetry as the ground state or not. The  $\text{CO}_2$  molecule was an example when symmetry is indeed broken at the core (O  $1s$ ) excited resonance state [7].

## DISCUSSION

The RXES spectra simulated in the frozen orbital approach are presented vertical bars in Figure 1. For a description of such simulations we refer to ref.[8]. Comparing to NRXES, the double peak structure of the two most intensive features in the C  $K$  emission case, is reduced to one peak ( $8t_{1u}(5\sigma)$ ), with the second feature (due to the  $1t_{2u}(1\pi)$  and  $7t_{1u}(1\pi)$  levels) forming a weak shoulder at the high energy side. The  $4\sigma$  ( $6t_{1u}$ ) band remains weak in the C  $K$  spectrum. For the O  $K$  spectrum, however, the transitions from the  $7t_{1u}(1\pi)$  and  $6t_{1u}(4\sigma)$  levels build up the two most intensive features.

It is worth noticing that the  $3d$  band ( $1t_{2g}$ ) level does not show up in the simulated resonant spectra, due to its gerade character. In the experimental O  $K$  RXES spectra, however, a very weak feature in the corresponding energy position can be observed (as indicated by an arrow in Figure 1). Because this feature is too far away (more than  $3.0$  eV) from its closest neighbour MO ( $8t_{1u}$ ), it should represent a separate state. A possible explanation could be the vibronic coupling effects of

the core excited state induce small admixtures of electronic symmetry-forbidden transition (here  $1t_{2g}$ ) in the RXES. It is notable that the similar feature is much weaker in the C *K* case.

## CONCLUSIONS

The purpose of this study was to investigate the notion of using a transition metal compound as a bridge between the free and the surface adsorbed species for the interpretation of these core electron spectroscopies. As we found in this investigation this notion forms a good starting point for analyzing the most salient features in all the spectra, while a detailed assignment makes it necessary to account for the particular electronic structure of the compound.

## ACKNOWLEDGEMENTS

T. Warwick is thanked for providing us some  $\text{Si}_3\text{N}_4$  windows which were used in the experiment.

## REFERENCES

1. L. Yang, H. Ågren, J.-H. Guo, C. S  the, A. F  lisch, A. Nilsson, and J. Nordgren, to be published.
2. T. Warwick, P. Heimann, D. Mossessian, W. McKinney and H. Padmore, Rev. Sci. Instr. **66**, 2037 (1995).
3. J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J. E. Rubensson and N. Wassdahl, Rev. Sci. Instr. **60**, 1690 (1989).
4. Custom-made window from Metrorex International Oy, P.O. Box 85, FIN.02201 Espoo, Finland.
5. V. Carravetta, L.G.M. Pettersson, H. Ågren, and O. Vahtras, Surf. Sci. **369**, 146 (1996).
6. P. Skytt, J.-H. Guo, N. Wassdahl, J. Nordgren, Y. Luo, and H. Ågren, Phys. Rev. A **52**, 3572 (1995).
8. Y. Luo, H. Ågren, and F.Kh. Gel'mukhanov, J.Phys B: At. Mol. Phys. **27**, 4169 (1994).

This work was supported by the Swedish Natural Science Research Council and the G. Gustafsson Foundation for Science and Medicine.

Principal investigator: E. Joseph Nordgren, Department of Physics, Uppsala University. E-mail: joseph@fysik.uu.se. Telephone: +46 18 4713554.